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CHEMICAL KINETICS OF EXCITED STATES. NOVEL APPLICATION OF GAS P--ETC(U)

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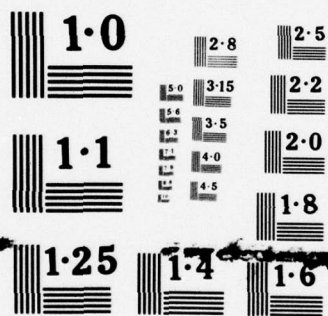
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Chemical Kinetics of Excited States,
Novel Application of Gas Phase EPR
and
Chemical Kinetics of Polyatomic Free Radicals.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Chemical kinetics research at Boston College is now proceeding in two major areas. One area involves the direct study of the kinetics of gas phase chemical reactions of metastable electronically excited atoms and molecules. In contract year 1976 we successfully demonstrated that Electron Paramagnetic Resonance (EPR) detection of metastable atoms in the gas phase can be combined with an electrical discharge-fast flow apparatus		

to obtain absolute rate constants for reactions of metastable atoms. The major thrust of this work during contract year 1977 has been to utilize the experimental capability which was developed in the first two years of this program. We have measured absolute reaction rate constants for the deactivation of metastable nitrogen atoms ($N^D_{3/2,5/2}$) by 17 different quenching partners, including O_2 , N_2O , CO_2 , H_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_8 , C_4H_{10} , C_5H_{12} , CH_3CHCH_2 , C_2H_2 , CH_3F , CF_4 , C_2F_6 , and SF_6 .

A second major project in our overall research effort was initiated during contract year 1977. An effort is being directed toward the development of new experimental techniques for the direct kinetics study of transient polyatomic free radical species such as CF_3 . During contract year 1977 we have successfully detected CF_3 radicals as products of an RF electrical discharge in mixtures of C_2F_6 and He. Low energy electron bombardment ionization coupled with Time-of-Flight Mass Spectrometry was employed in the detection of these radicals.

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Summary

Chemical kinetics research at Boston College is now proceeding in two major areas. One area involves the direct study of the kinetics of gas phase chemical reactions of metastable electronically excited atoms and molecules. In contract year 1976 we successfully demonstrated that Electron Paramagnetic Resonance (EPR) detection of metastable atoms in the gas phase can be combined with an electrical discharge-fast flow apparatus to obtain absolute rate constants for reactions of metastable atoms. The major thrust of this work during contract year 1977 has been to utilize the experimental capability which was developed in the first two years of this program. We have measured absolute reaction rate constants for the deactivation of metastable nitrogen atoms ($N^2D_{3/2,5/2}$) by 17 different quenching partners, including O_2 , N_2O , CO_2 , H_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_8 , C_4H_{10} , C_5H_{12} , CH_3CHCH_2 , C_2H_2 , CH_3F , CF_3H , CF_4 , C_2F_6 , and SF_6 .

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Progress in Research Program During 1977

A. Electron Spin Resonance (ESR) - Flow Kinetics

One goal of our original proposal was to demonstrate that the ESR-discharge flow technique could be used to measure rate constants for metastable atom quenching reactions. During 1977 we have realized this goal by measuring absolute quenching rates for seventeen reaction systems involving metastable N atoms. These include both systems which have been previously studied by other methods (in order to check for possible systematic errors) and new systems for which comparative data is unavailable.

The flow tube apparatus is diagrammed in fig. 1. A known flow of N_2 and He is discharged to produce the metastable N atoms ($^2D_{3/2,5/2}$). Reactant gas and SF_6 (to

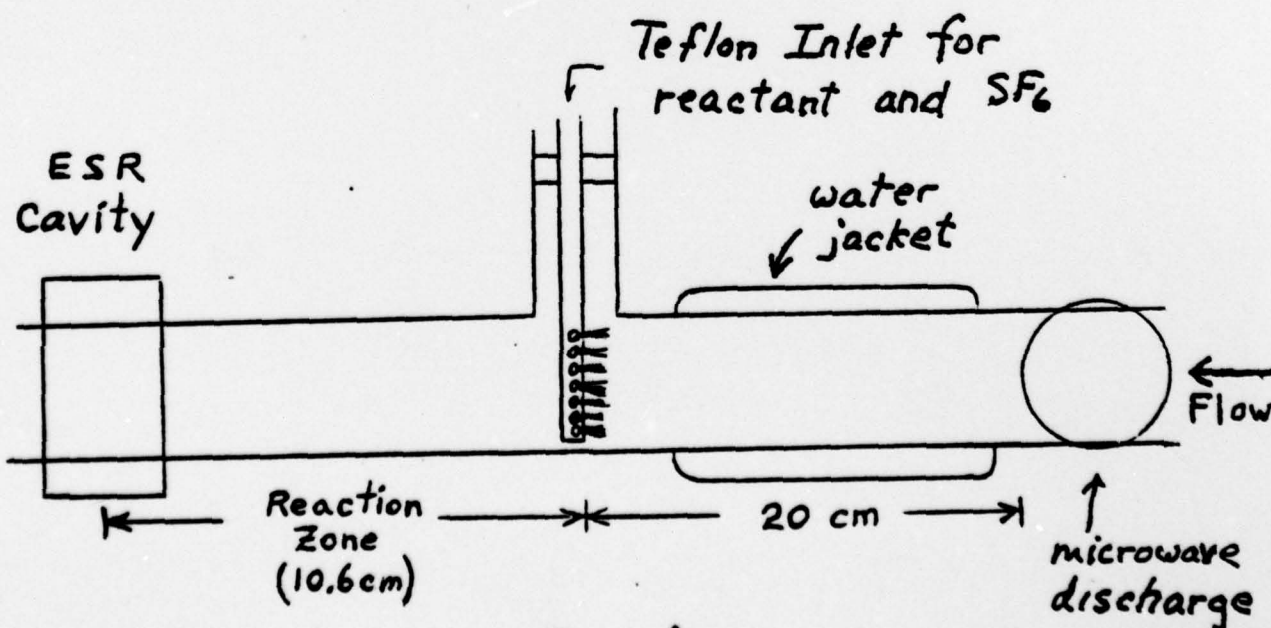


Fig. 1

suppress electron noise) are introduced through the teflon reactant inlet which is a 1/8" dia. teflon tube perforated with approximately 20 small holes pointing upstream. Rate constants are obtained from measurements of $N(^2D_{5/2})$ ESR signal intensities versus the concentration of reactant gas in the flowtube. The details of these experiments will be described in a future publication (J. Chem. Phys.).

The results of our measurements are summarized in Tables I and II. Table I presents data on systems for which comparative values are available in the literature. The values in Table II represent first determinations. In choosing these systems for study we were motivated in part by the desire to obtain results for a series of similar reactions so that relationships between structure and reactivity might be investigated. For a series of hydrocarbons the length of the carbon chain has been varied. The effect of double and triple bonds in the hydrocarbon has been studied, and the effect of fluorine substitution for hydrogen in a series of fluorinated hydrocarbons has been investigated. These results will be compared with existing models and theories of quenching reactions.

During the final quarter of 1977 we initiated work on the detection of $O(^1D_2)$ and $N(^2P_J)$. We have found in our studies of $N(^2D)$ that cooling the microwave discharge results in a significant increase in the $N(^2D)$ signal. We have constructed a flowtube which can be cooled to 77° K using liquid nitrogen.

TABLE I. Rate Constants (cm^3/sec) for reactions of $\text{N}(^2\text{D})$ with various gases

Reactant	Lin & Kaufman	Black et. al.	This work
O_2	4.5×10^{-12}	7×10^{-12}	4.5×10^{-12}
N_2O	2.2×10^{-12}	3×10^{-12}	2.4×10^{-12}
CO_2	2.6×10^{-13}	6×10^{-13}	5.2×10^{-13}
H_2		5×10^{-12}	2.7×10^{-12}
CH_4		3×10^{-12}	3.5×10^{-12}
C_2H_4		1.2×10^{-10}	0.60×10^{-10}

References: C.-L. Lin and F. Kaufman, J. Chem. Phys. 55, 3760 (1971).

G. Black, T.G. Slanger, G.A. St. John, and R.A. Young, J. Chem. Phys. 51, 116 (1969).

TABLE II. Rate Constants (cm^3/sec) for reactions of $\text{N}(^2\text{D})$ with various gases

Experiment Number	Reactant				
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
	methane	ethane	n-propane	n-butane	neo-pentane
1	3.3×10^{-12}	2.3×10^{-11}	3.7×10^{-11}	4.5×10^{-11}	3.6×10^{-11}
2	3.7×10^{-12}	2.0×10^{-11}	3.1×10^{-11}	4.2×10^{-11}	3.5×10^{-11}
3	3.4×10^{-12}	2.0×10^{-11}	3.3×10^{-11}	4.7×10^{-11}	3.9×10^{-11}
4	3.2×10^{-12}	2.2×10^{-11}	3.3×10^{-11}	4.4×10^{-11}	3.6×10^{-11}
5	4.0×10^{-12}	2.3×10^{-11}	3.8×10^{-11}	5.6×10^{-11}	3.6×10^{-11}
6	3.0×10^{-12}	2.0×10^{-11}	3.7×10^{-11}	4.0×10^{-11}	3.3×10^{-11}
7	3.7×10^{-12}	2.2×10^{-11}		3.7×10^{-11}	2.9×10^{-11}
8		1.8×10^{-11}		2.3×10^{-11}	
9				2.6×10^{-11}	
Average	3.5×10^{-12}	2.1×10^{-11}	3.5×10^{-11}	4.0×10^{-11}	3.5×10^{-11}
	$\text{CH}_2=\text{CH}_2$	$\text{CH}_3\text{CH}=\text{CH}_2$	$\text{CH}\equiv\text{CH}$	CH_3F	CF_3H
1	5.0×10^{-11}	11.6×10^{-11}	11.5×10^{-11}	1.2×10^{-12}	0.9×10^{-13}
2	7.3×10^{-11}	11.0×10^{-11}	9.8×10^{-11}	0.68×10^{-12}	1.2×10^{-13}
3	6.8×10^{-11}	5.6×10^{-11}		1.1×10^{-12}	1.3×10^{-13}
4	5.7×10^{-11}	4.3×10^{-11}		1.3×10^{-12}	1.0×10^{-13}
5	5.0×10^{-11}	9.6×10^{-11}		0.9×10^{-12}	1.2×10^{-13}
6		5.6×10^{-11}		1.8×10^{-12}	1.3×10^{-13}
7		8.9×10^{-11}		1.2×10^{-12}	1.3×10^{-13}
8		13.3×10^{-11}			1.5×10^{-13}
9		9.2×10^{-11}			1.4×10^{-13}
Average	6.0×10^{-11}	8.8×10^{-11}	10.6×10^{-11}	1.2×10^{-12}	1.2×10^{-13}

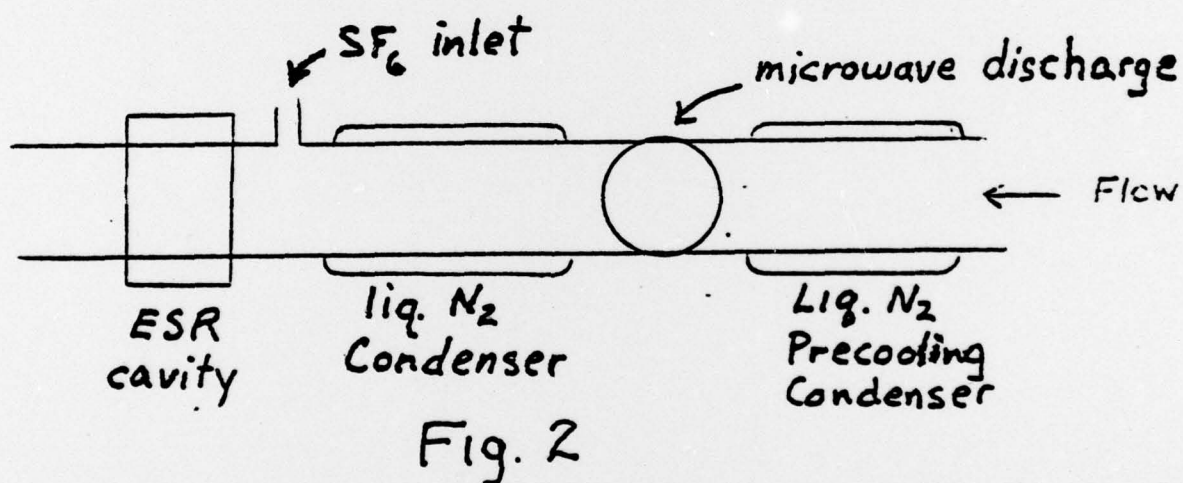
Table II con't.

There is no detectable quenching of $N(^2D)$ by the following gases:

CF_4 , C_2F_6 , and SF_6 the rate constant must be less than 10^{-14} cc.sec $^{-1}$

Additional experiments on $CH_2=CH_2$ and $CH\equiv CH$ are in progress at the time of this writing.

There is evidence that $O(^1D_2)$ and $N(^2P_J)$ are produced in sufficiently large concentrations in flow discharges and that the problems of detection are associated in large part with wall deactivation. Cooling the walls to 77°K should increase the production of atomic species, reduce the rate of wall deactivation, and increase condensation of molecular impurities which can lower the metastable signals by means of unwanted quenching reactions. Fig. 2 shows a schematic drawing of this flowtube.



B. Polyatomic Free Radical Kinetics by Mass Spectrometry

Electric discharge-fast flow techniques coupled with detection by kinetic spectroscopy have been used extensively to study reactions of free atoms and to some extent of diatomic free radicals. We have initiated a program to extend the application of these techniques to the study of polyatomic free radicals. In order to accomplish this end two experimental problems must be solved. First, relatively pure free radical sources, uncomplicated by atom or radical

impurities, are needed. Second, unambiguous methods of detection for polyatomic free radicals are necessary so that the steady state concentration of the radicals can be monitored.

Our work in this area began during this past contract year, 1977, and the initial studies have focused on the production and detection of trifluoromethyl radicals, CF_3 . Our approach is to develop a simple, clean, and relatively inexpensive source of CF_3 radicals in the gas phase and to investigate at least three techniques for the direct measurement of the radical concentration. Selected reactions of CF_3 will be studied subsequently. The first source of radicals to be investigated is an RF electrical discharge through a flowing mixture of C_2F_6 and He gas. There is indirect evidence that this source will meet the requirements stated above (R.J. Lagow et.al. J. Amer. Chem. Soc. 97, 518 (1975)), but CF_3 radicals have not previously been detected directly from such a source. During this past year we have accomplished the detection of CF_3 radicals from this source using electron bombardment mass spectrometry. The essential feature to note in these experiments is that the electron energy in the ion source of the mass spectrometer was only 13 eV. Although operating at low electron energy means a significant loss in sensitivity for CF_3 radical detection, it also eliminates spurious signals which result from fragmentation of stable species in the ion source. This point is expanded in a following paragraph.

A schematic diagram of the RF discharge source and the time-of-flight mass spectrometer ion source is shown in Fig. 3.

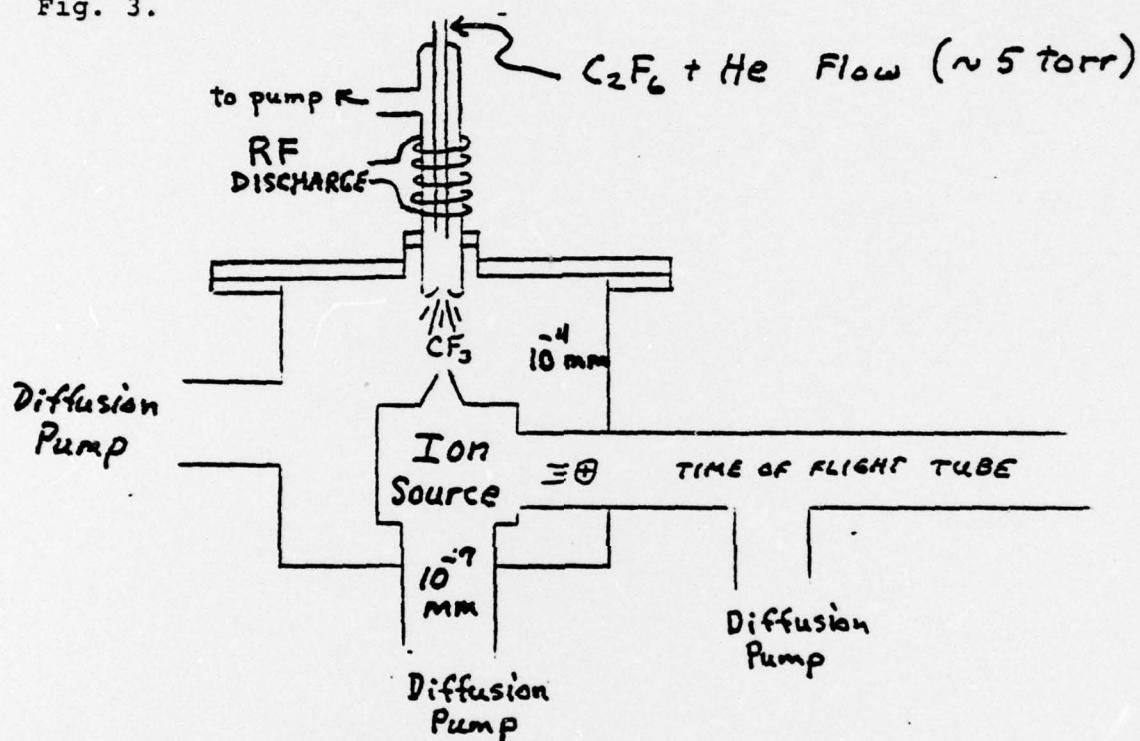
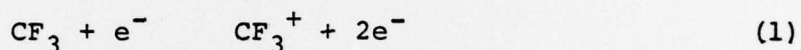


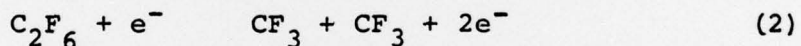
Fig. 3

Three versions of the RF discharge source were designed, constructed, and tested during 1977. Typical operating conditions are shown in the figure. The mass spectrometer is a commercial unit, Bendix model 3012, which we have used without significant modification. Before presenting our results we will discuss the problems associated with electron bombardment ionization and how these problems can be avoided by limiting the electron bombardment energy.

The essential problem encountered in the detection of CF_3 radicals by electron bombardment ionization mass spectrometry is that of fragmentation. The desired signal is a current of CF_3^+ ions which is produced by ionization of CF_3 in the ion source as in equation (1).



The ionization potential of CF_3 is 10.2 eV. If high energy electrons are used to ionize the radicals (70-100 eV) the efficiency of the ionization process (Eq. 1) is maximized but an additional spurious source of CF_3^+ is also present due to the process of fragmentation represented in Eq. 2.

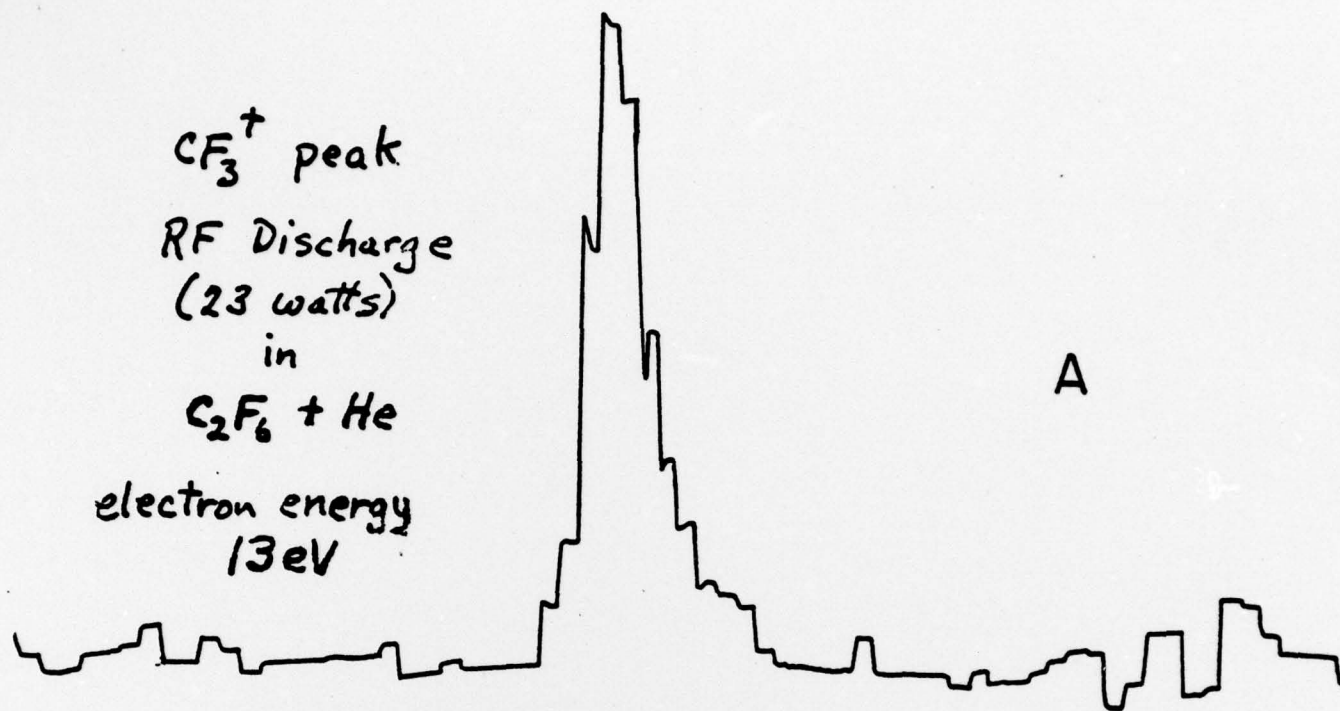


At 70-100 eV electron energy this latter process dominates the former since the concentration of undissociated C_2F_6 is much larger than the CF_3 radical concentration. Therefore the detection of a CF_3^+ signal in the mass spectrum does not necessarily indicate the production of CF_3 radicals in the flow tube. Since the appearance potential of CF_3^+ from the fragmentation of C_2F_6 as in Eq. 2 is approximately 14.5 eV, this source of CF_3^+ signal can be suppressed if the electron energy is lowered below 14.5 eV. For example, if the electron energy is adjusted to 13 eV, there is sufficient energy to ionize the CF_3 radicals but not to fragment C_2F_6 . Therefore,

the CF_3^+ signal at this electron energy comes exclusively from the ionization of CF_3 radicals. Unfortunately the ionization efficiency drops drastically as the electron energy is lowered so there is a reduced detection sensitivity at low electron bombardment energy. In our experiments we have made up for this loss of sensitivity by signal averaging the output of the mass spectrometer using a PAR Waveform Educator which accumulates the signal from multiple mass scans and averages out the noise.

The results of CF_3 radical detection are shown in Fig. 4. The operating conditions are recorded in the figure. Each trace is the result of 60 mass scans accumulated over a 3 minute period. The upper trace shows a single mass peak at $m/e = 69$, the mass of CF_3 . The lower trace shows the affect of turning off the RF discharge and scanning for 3 minutes through the same mass range. The signal also disappears when the discharge is ~~low~~ on but the C_2F_6 flow is turned off. These spectra were obtained at an electron energy of 13 eV. So far we have detected CF_3 radicals with an electron energy as low as 11.5 eV, only 1.4 eV above the appearance potential for CF_3^+ from CF_3 .

In summary, we have successfully completed the initial phase of this research program by showing that direct measurement of CF_3 radical production can be accomplished using low energy electron bombardment ionization mass spectrometry. Initial measurements indicate that an RF electrical discharge in C_2F_6 and He is an efficient source of CF_3 radicals which can be used for kinetic studies.



same mass scan as A
RF Discharge OFF

B



Fig 4

Recent Publications

- *Observation of the Opto-Acoustic Effect in the Microwave Region, G.J. Diebold and D.L. McFadden, Applied Phys. Letters, 29, 447 (Oct. 1, 1976).

The microwave analog of the optoacoustic effect was observed. Collisional relaxation of absorbed microwave energy between magnetic sublevels of gaseous molecular oxygen results in the production of an acoustical signal which is detected by a sensitive microphone.

- *Kinetics of the $O + F_2$ Reaction: A Case of Low Reactivity of Elemental Fluorine, R.H. Krech, G.J. Diebold, and D.L. McFadden, J. Am. Chem. Soc. 99, 4605 (1977).

This gas phase reaction was studied by the EPR-Discharge Flow Technique. The rate constant obtained is given by the Arrhenius equation, $k = 10^{12.99} \exp[-10,4/RT] \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$. The large activation energy for the reaction is attributed to the low polarizability of molecular fluorine.

- *An Empirical Correlation of Activation Energy with Molecular Polarizability for Atom Abstraction Reactions, R.H. Krech and D.L. McFadden, J. Am. Chem. Soc. 99, 8402 (1977). Activation energies for a homologous series of exoergic atom transfer reactions are shown to correlate inversely with molecular polarizability. Sixty-five reactions are presented. Predictions of activation energies for some reactions are included.

Manuscripts in Preparation

*Signal/Noise Enhancement in Gas Phase EPR Studies of Atomic Nitrogen and Rare Gas Metastables, G.J. Diebold and D.L. McFadden (to be submitted to J. Chem. Phys.).

*Gas Phase Chemiluminescence in Alkali Halid Systems, D.L. McFadden, to appear in a book on the chemistry of alkali halide vapors, Academic Press, 1978.

*Absolute Rate Coefficients for the Quenching of Metastable Nitrogen Atoms ($N^2D_{3/2,5/2}$) by Several Molecules, I.V. Rivas, B. Fell, and D.L. McFadden (J. Chem. Phys.).

*Acknowledgment is made to ONR for partial support of this work.

D.L. McFadden received an Alfred P. Sloan Research Fellowship for 1977-1979.

Additional Work

Chemiluminescent Reactions of Boron with Alkali Fluorides,
U.C. Sridharan, D.L. McFadden, and P. Davidovits,
J. Chem. Phys, 65, 5373 (1976).

Chemiluminescence from the Gas Phase Reaction of Atomic
Boron with the Alkali Metal Fluorides, U.C. Sridharan,
D.L. McFadden, and P. Davidovits, ACS Symposium Ser.
56, 136 (1977).

Chemiluminescence from the Gas Phase Reaction of Atomic
Carbon with PbO, U.C. Sridharan, T. DiGiuseppi, D.L.
McFadden and P. Davidovits (to be submitted to J.
Chem. Phys.).

The Alkali Halide Vapors, P. Davidovits and D.L. McFadden, eds.,
Academic Press, New York, 1978.

Rate Coefficients for the Reactions, $B + O_2 \rightarrow BO + O$ and
 $Al + N_2O \rightarrow AlO + N_2$ Using a Diffusion Technique,
U.C. Sridharan, T.G. DiGiuseppi, D.L. McFadden, and
P. Davidovits (To be submitted to J. Chem. Phys.).

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